LIGNIN PYROLYSIS IN HEATED GRID APPARATUS: EXPERIMENT AND THEORY

Eitan Avni and Robert W. Coughlin

University of Connecticut, Storrs, CT 06268

Peter R. Solomon and Hsiang Hui King

Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108

Introduction

The study of lignin pyrolysis has a vital importance since all lignin conversion processes, namely; combustion, liquefaction and gasification, are initiated by this step. Lignin, a major component of biomass is a potential source of aromatic chemicals through the pyrolysis process. Important recent reviews of lignin conversion processes have been published by Goldstein (1), Drew (2), Goheen (3) and Coughlin and Avni, et.al., (4).

Very few kinetic studies of lignin pyrolysis have been carried out recently. Gavslss, et.al., (5) studied the pyrolysis of Kraft lignin using the captive sample technique. At 400–650°C for 10–120 sec, he claimed that a fundamental kinetic description of lignin pyrolysis was not possible at the time. Klein (6) modeled lignin pyrolysis based on its model components and compared his simulations to previously published data (7). In a recent study by Avni, et.al., (8–9), the pyrolysis behavior of Iotech lignin was studied at different ambient pressures and heating rates.

This paper considers the application of a recently developed pyrolysis model of coal pyrolysis (10–12) applied to a heated grid as well as an entrained flow reactor, to the pyrolysis of lignin. Flash pyrolysis as well as slow heating rate pyrolysis was carried out in a heated grid (13), in which on-line, in-situ gas and tar analysis is performed by Fourier Transform Infrared (FT-IR) Spectroscopy. The model has proved to be successful in simulating the results of vacuum flash pyrolysis and slow heating rate pyrolysis for a variety of lignins.

Experimental

Lignin Samples

Seven lignins were used in the study; Table 1 compares the different lignins and their sources. Four of them were received from manufacturers while the last three were extracted in our laboratory. Table 2 shows the elemental composition and methoxy content of the lignins. All lignin samples were dried for 48 hours at 108°C under vacuum before the experiments.

Flash Pyrolysis Experiments

The flash pyrolysis apparatus is illustrated in Fig. 1. It consists of a heated grid pyrolyzer located in the center of a large gas cell with KBr windows to allow FT-IR (Nicolet) analysis (13). The lignin is evenly distributed between two layers of stainless-steel or tungsten screen which is electrically heated. Lignin temperatures of 1800°C and heating rates in excess of 10,000°C/sec for the highest temperatures can be achieved using a tungsten screen. When flash pyrolysis is performed in vacuum, the tar molecules quickly escape the grid and land on the cold glass.

Evolution kinetics for gaseous species are determined with the FT-IR which permits low resolution spectra (8 wavenumbers) to be taken at 80 msec intervals. The low resolution analysis can determine CO, CO_2, H_2O, CH_4, SO_2, CS_2, C_2H_2, C_2H_4, C_3H_6, benzene, and heavy paraffins and olefins. The time-temperature evolution for

307

each species can be determined from such scans as indicated in Fig. 2 which shows
the CO yield as a function of time at several temperatures.

The distribution of major products is determined by weighing the lignin, the
char (which remains on the screen) and the tar (which accumulates on a glass tube
surrounding the grid) and by quantitative analysis of 0.5 wavenumber, FT-IR spectra
of the evolved gas taken at the completion of a run. The high resolution spectra
can quantitatively determine all of the above species plus C_2H_6, C_3H_8, C_4H_8, NH_3
and potentially many other species which have not yet been observed. Calibration
of the FT-IR was made using pure gases or prepared gas mixtures. Analysis of the
solids was performed with the FT-IR and by elemental analysis.

Constant Heating Rate Experiment

Slow constant heating rate experiments with evolved gas analysis by Mass
Spectrometry (MS) or Gas Chromatography (GC) has been used by several investigators
to study coal (14-17). Gas analysis by FT-IR, as used in the experiments here,
offers advantages over GC in speed and over MS in the ability to identify heavy tar
materials.

Constant heating rate experiments were performed for lignin using the apparatus
shown in Fig. 1. The sample is heated at a constant rate (30°C/min) while gas
evolution is monitored by FT-IR. The pyrolysis gas is swept from the cell with a
constant flow of nitrogen (700 ml/min) at a pressure of 1 atm.

Pyrolysis Model

The pyrolysis model assumes a lignin structure consisting of substituted
phenyl-propane subunits linked by C-O and C-C bonds. During thermal decomposition
the relatively weak bonds break, releasing the tar which is comprised of monomers,
dimers and trimers of phenyl-propane subunits. The FT-IR spectra of the lignin tar
show a remarkable similarity to the parent lignin. Figure 3a-c shows such a
comparison. Such similarity has also been observed for pyrolysis of coals and model
polymers.

A pyrolysis model should simulate the evolution of tar fragments and
competitive cracking of substituted groups and ring clusters to form the light
molecular species of the gas. The yield of each gas species should depends on the
functional group distribution in the original lignin. At low temperatures there is
very little rearrangement of the lignin polymer but there is decomposition of the
substituted groups and aliphatic structures resulting in CO_2 release from the
carbonyl, H_2O from hydroxyl, hydrocarbon gases from aliphatic and methoxy groups,
and CO from weakly bound oxygen groups such as aldehyde groups. At high
temperatures there is breaking and rearrangement of the aromatic rings. Late in the
pyrolysis, the rearrangment of the lignin subunits permits H_2 to be evolved from the
aromatic hydrogen. Additional CO form tightly bound oxygen functionalities. As
this process continues the char becomes more graphitic. At high temperatures the
FT-IR spectra of lignin char and coal char are remarkably similar, (see Figure 3d)
both are highly aromatic. A striking feature of thermal decomposition which was
observed for a variety of coals and lignins in the heated grid experiments is that
the temperature dependent evolution rate of CO_2 and CO are similar for all lignins
and coals while the evolution rates of H_2O, CH_4, paraffins and tar from lignin vary
slightly from coal, due to the different bridges between the ring clusters. The
rate of evolution of a specie will depend on the nature of the functional group
which is its source but appears relatively insensitive to lignin source or
extraction processes. The insenitivity of kinetic rates to coal rank has been
reported in other investigations (14,18-21).

The mathematical description of the pyrolysis used here has been presented
previously (10-12). The model considers the removal of functional groups by a
parallel independent evolution of the light species in competition with the tar
evolution.

To model these two competing paths with one path yielding a product which is
similar in composition to the parent coal, the dry, ash-free (DAF) coal or lignin is

represented as a rectangular area. As shown in Fig. 4a, the Y dimension is divided according to the chemical composition of the coal or lignin. Y°_i represents the initial fraction of a particular component (carboxyl, aromatic hydrogen, etc) and the sum of the Y°_i's equals 1. The evolution of each component into the gas (carbonxyl into CO_2, aromatic hydrogen into H_2, etc) is represented by the first order diminishing of the Y_i dimension, $Y_i=Y^\circ_i exp(-k_i t)$. The X dimension is divided into a potential tar forming fraction X° and a non-tar forming fraction $1-X^\circ$. The evolution of the tar is represented by the first order diminishing of the X dimension $X=X^\circ exp(-k_t t)$.

Figure 4-a shows the initial state of the coal. Values for Y° are obtained from elemental and FT-IR analysis and from the heated grid pyrolysis experiments (10,12,22). The value of X° is at present a parameter of the model. It is controlled by the oxygen and aliphatic or hydroaromatic hydrogen content of the lignin and can be influenced by pressure, particle size, bed geometry and the transport properties of the pyrolysis medium.

Figure 4-b shows the initial stage of thermal decomposition during which the volatile components, H_2O, CO-loose and CO_2, evolve from the hydroxyl, ether-loose and carboxyl groups, respectively, along with aliphatics and tar. At a later stage (Fig. 4-c) CO-tight and H_2 are evolved from the ether-tight and aromatic hydrogen. Figure 4-d shows the final state of the char, tar and gas.

Table 3 presents the kinetic rates used in the model and the functional group composition of Iotech Aspen lignin. A distributed activation energy is used for species evolution kinetics. Such models were used by Pitt (23) and by Anthony, et.al. (24) for describing coal weight loss. Weimer and Nagan (14) employed Anthony's model to describe individual species evolution. This model was used in the present study.

Results and Discussion

Figure 5 shows the evolution rates of the major gas species and tar from Iotech lignin at a constant heating rate pyrolysis of 30°C/min. The simulations of the evolution rates, using the parameters in Table 3 agree well with the experimental results. As was mentioned previously, the kinetic rates of CO and CO_2 are similar for coal and lignin. The experimental CO evolution rates (Fig. 6) of several lignins indicate a high temperature tight-CO and show the insensitivity of the evolution rate to the lignin sources or the extraction processes used there.

The methane evolution rate suggests a tightly and loosely bound precursor. The loose methane is probably from the methoxy group of the phenylpropane subunit. The methoxy content of Iotech lignin is 17.01 weight percent, much higher then any coal methoxy content. Figure 8 compares the experimental evolution rate of methane from Iotech lignin and Pittsburgh Seam coal, the only difference between the two is the loose methane in the lignin. The similarity between the two can be explained in light of the similar FT-IR spectra (see Fig. 3-d) of lignin char and coal char at 500°C and higher temperatures. In both cases the char is highly aromatic relative to the starting materials. The relative ratio of the area under the aliphatic peaks near 2900 cm^{-1} to the aromatic peaks near 800^{-1} decreased drastically in the lignin char at 500°C compared to the ratio in the lignin. In both coal and lignin the residual oxygen appears to be predominantly ether type oxygen. Figure 7 compared the methane evolution rate of several lignins, again the rate is insensitive to the lignin source and extraction process. The ratio of the loose methane to tight methane peaks is changing from one lignin to another. The ratio seems to increase with an increase in the methoxy content of the lignin (see Table 2 for methoxy content).

The predicted tar evolution rate is in excellent agreement with the experimental data. The activation energy used for the simulations of tar evolution (48 kcal/mole + 1500 cal/mole) is in a very good agreement with the estimated activation energy of the ether linkage (48 kcal/mole) connecting the phenylypropane subunits. The activation energies have been calculated using the group additivity theory of S. W. Benson (25,26). The DTGA of Iotech lignin confirms the location and shape of the tar rate curve on the temperature scale. The differences in the tar rates between

coal and lignin are due to the weak ether linkages that exist in the lignin between the polymer subunits; such weak linkages do not exist in coal.

Figure 9 shows the gas yield versus pyrolysis time in a flash pyrolysis. The major gas species evolved were CO, CO_2, H_2O and paraffins, at a final static temperature of 500°C for 80 seconds. The simulations of the gas species obtained with the parameters in Table 3 are in good agreemet with the data presented within the experimental errors. The methane evolution in the slow heating rate experiments shows a higher fraction of tight-methane than is observed in the flash pyrolysis. There is no such indication with the rest of the gas species.

Yield of CO versus pyrolysis time in a flash pyrolysis at different temperatures of flash pyrolysis are shown in Fig. 2 where it is evident that the agreeement between theory and experiment is good.

Conclusions

The experiments have shown that lignin pyrolysis kinetics are insensitive to lignin source or extracting process. Theory and experiment agree well for both slow and fast heating rates, using the given model parameters. The lignin parameters of the model are related to the functional group composition of the lignin.

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TABLE 1

LIGNIN SOURCE

Lignin	Wood	Manufacturer	Pretreatment
Iotech	Aspen	Iotech Corp.	steam explosion
Stake	Aspen	Stake Tech. Ltd.	autohydrolysis
BEC	Aspen	Biological Energy Corp.	---
Indulin	Pine	Westvaco	---
Ethanol	Aspen	b	[a] steam explosion
HCl	Aspen	c	[a] steam explosion
H_2SO_4	Aspen	d	[a] steam explosion

a) The Aspen wood was steam-exploded by Iotech Corp. and extracted in our laboratory.

b) 25 g of wood is mixed with 250 g of 43 Wt% ethanol in water mixture at pH 6. The reaction is carried out in autoclave at 185°C for 1 hour.

c) 25 g of wood was stirred for 4 hours with 500 g conc. HCl at room temperature. After 20 hours water is added and the mixture is filtered and washed with soda solution.

d) 25 g of wood is treated with 250 ml of 72% H_2SO_4 and stirred at room temperature for 2 hours, 2 volumes of water is added and the mixture is filtered. The lignin is reflex for 1 hour in 125 ml 3% H_2SO_4.

TABLE 2

ELEMENTAL COMPOSITION AND METHOXY CONTENT OF LIGNINS

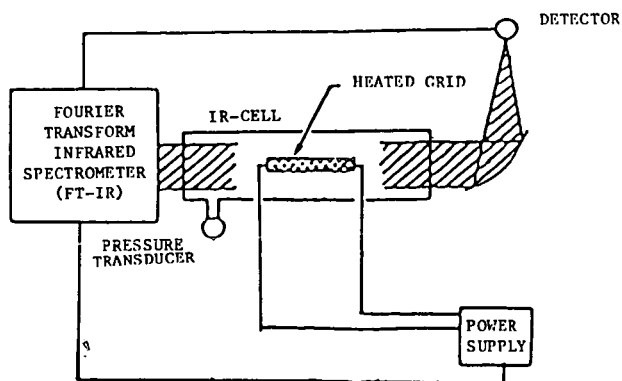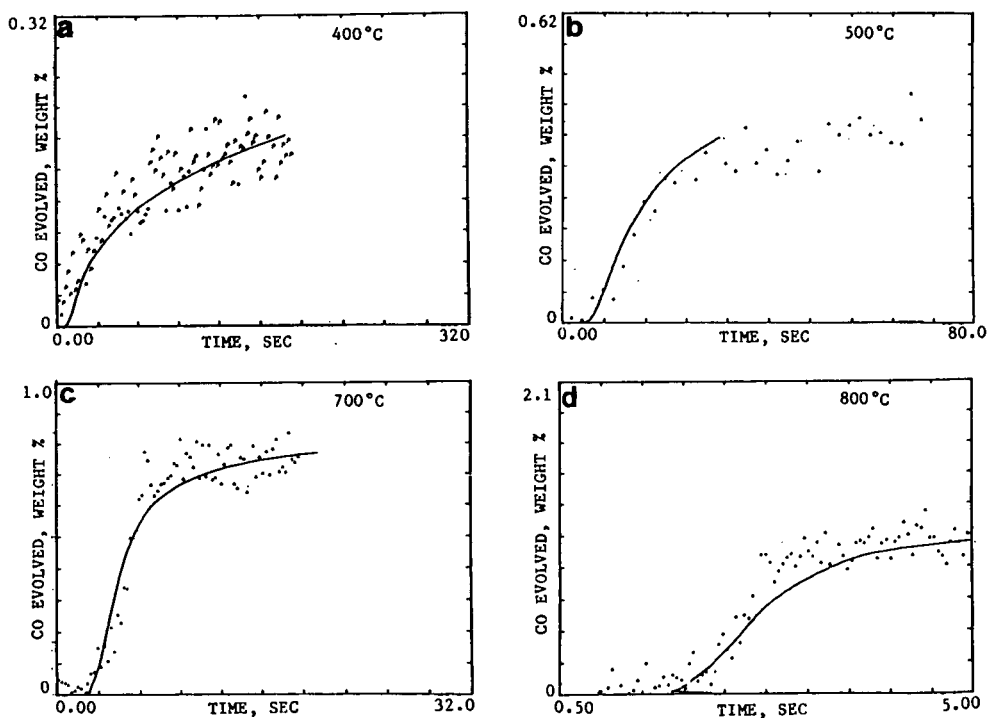| Lignin	Iotech	Indulin	BEC	Stake	Ethanol	HCl	H_2SO_4
C	63.44	64.35	66.84	60.61	65.57	52.33	61.54
H	5.87	5.71	6.09	5.31	5.76	5.75	5.14
O	29.94	27.69	27.04	33.39	28.37	40.08	31.83
S	-	1.3	-	-	-	-	0.5
Mineral	0.75	0.95	0.03	0.69	0.30	0.56	0.99
Methoxyl	17.01	13.95	19.32	12.58	17.41	6.93	10.99

Figure 1. Pyrolysis Apparatus.

Figure 2. CO Yield from Iotech Lignin at Different Temperatures of Flash Pyrolysis, (points) experiment and (solid line) simulation.
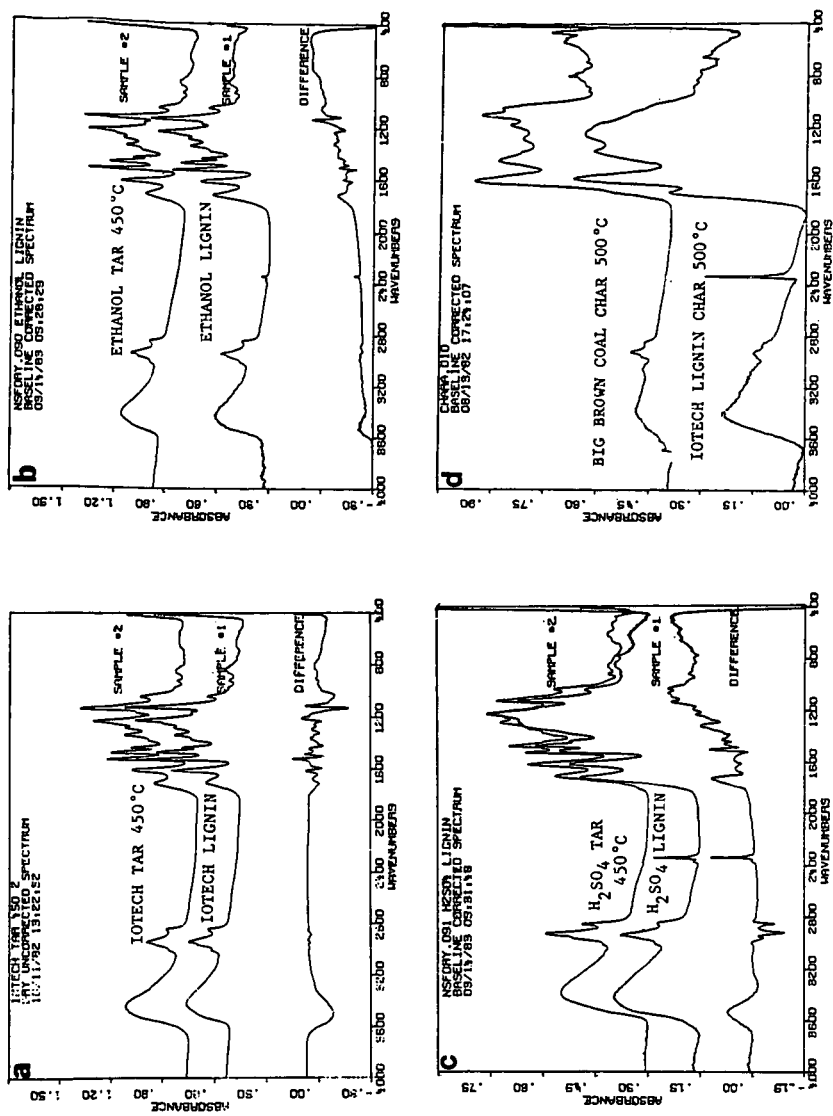
Figure 3. Infrared Spectra showing Comparison of Lignin and Tar as well as Coal Char and Lignin Char.

313

TABLE 3

Kinetic Rates and Functional Group Compositions

Composition Parameter		Iotech Lignin (WT DAF)		Kinetic Rate Constants (sec^{-1})
C		0.634		
H		0.059		
N		0.000		
S(organic)		0.000		
O		0.307		
		1.000		
r_1	CO_2 - Extra-loose	0.0068	k_1	$= 0.10E+15 \exp((23900. \pm 2500.)/T)$
r_2	CO_2 - Loose	0.0036	k_2	$= 0.10E+15 \exp((27900. \pm 1400.)/T)$
r_3	CO_2 - Tight	0.0026	k_3	$= 0.10E+15 \exp((32900. \pm 3300.)/T)$
r_4	H_2O	0.0654	k_4	$= 0.10E+14 \exp((23000. \pm 2000.)/T)$
r_5	CO - Ether Loose	0.0300	k_5	$= 0.17E+12 \exp((25000. \pm 2500.)/T)$
r_6	CO - Ether Tight	0.3889	k_6	$= 0.10E+16 \exp((54900. \pm 5000.)/T)$
r_7	HCN - Loose	0.0000	k_7	$= 0.54E+04 \exp((8850. \pm 0.)/T)$
r_8	HCN - Tight	0.0000	k_8	$= 0.70E+08 \exp((12000. \pm 0.)/T)$
r_9	NH_3	0.0000	k_9	$= 0.12E+13 \exp((27300. \pm 2400.)/T)$
r_{10}	CH_x-Aliphatic	0.0942	k_{10}	$= 0.17E+15 \exp((30000. \pm 1500.)/T)$
r_{11}	Methane-loose	0.0049	k_{11}	$= 0.50E+16 \exp((30000. \pm 1500.)/T)$
r_{12}	Methane-tight	0.0100	k_{12}	$= 0.20E+14 \exp((30000. \pm 3000.)/T)$
r_{13}	H-Aromatic	0.0130	k_{13}	$= 0.16E+08 \exp((23000. \pm 2300.)/T)$
r_{14}	C-Non Volatile	0.3804	k_{14}	$= 0$
r_{15}	S-Organic	0.0000		
	Total	1.0000		
r^0	Tar	0.6200	k_T	$= 0.10E+15 \exp((24000. \pm 1500.)/T)$

Cracking Rates:

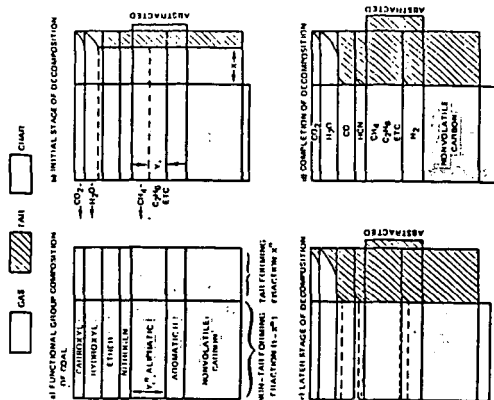|		
Paraffins - Olefins	k_{OL}	$= 0.15E+12 \exp((27600.)/T)$
Olefin - Acetylene	k_{AC}	$= 0.21E+08 \exp((22000.)/T)$

*Distributed rates have not yet been determined.

Figure 4. Progress of Thermal Decomposition According to Model. a) Functional Group Composition of Lignin, b) Initial State of Decomposition, c) Later Stage of Decomposition, d) Completion of Decomposition.
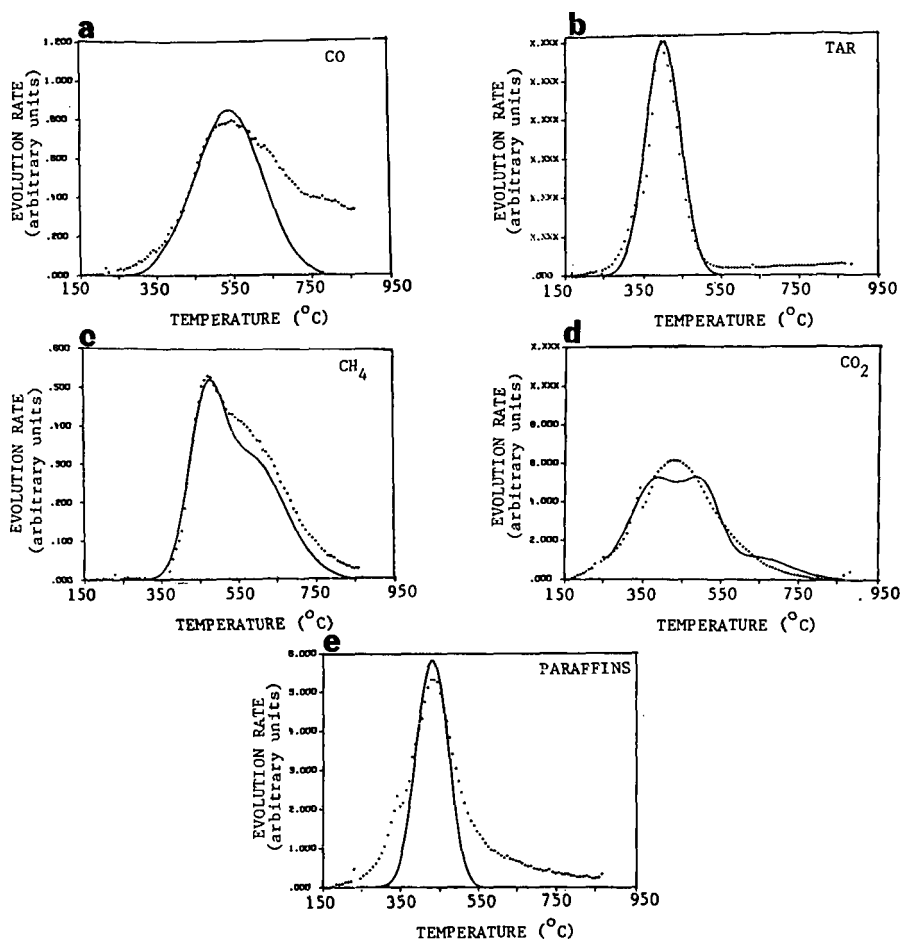
Figure 5.   Evolution Rate of Major Volatile Species from Iotech Lignin in a
Heating Rate of 30°C/min, Experiment (points) and Simulations
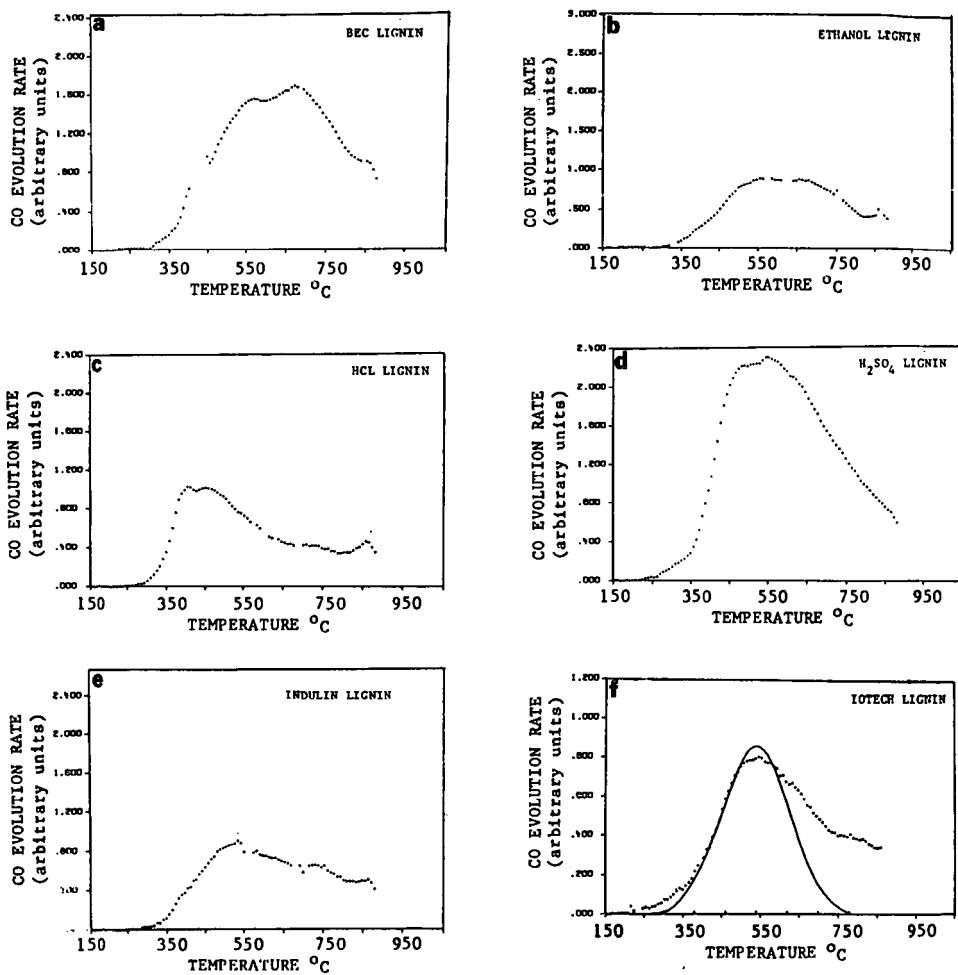(solid line).

Figure 6. Evolution Rate of CO from Different Lignins at a Heating Rate of 30°C/min, experiment (points) and simulation (solid line).
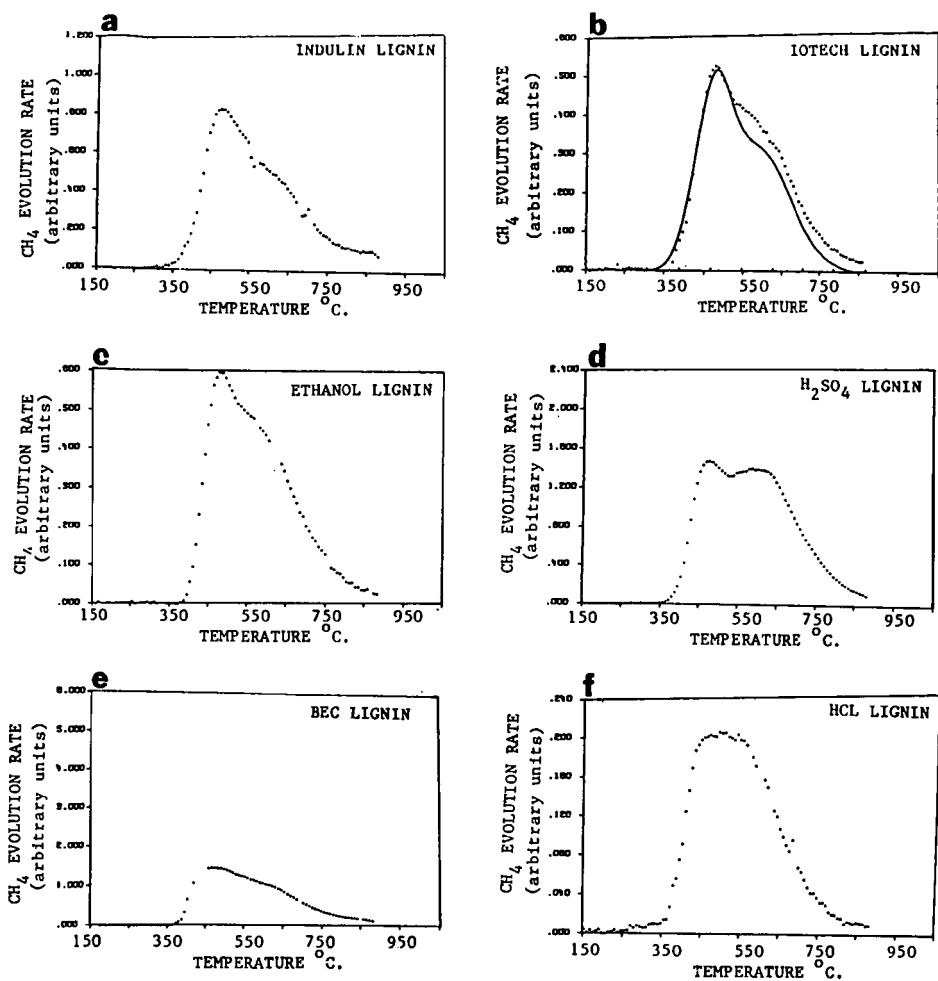
Figure 7. Evolution Rate of Methane from Different Lignins at a Heating Rate of 30°C/min.
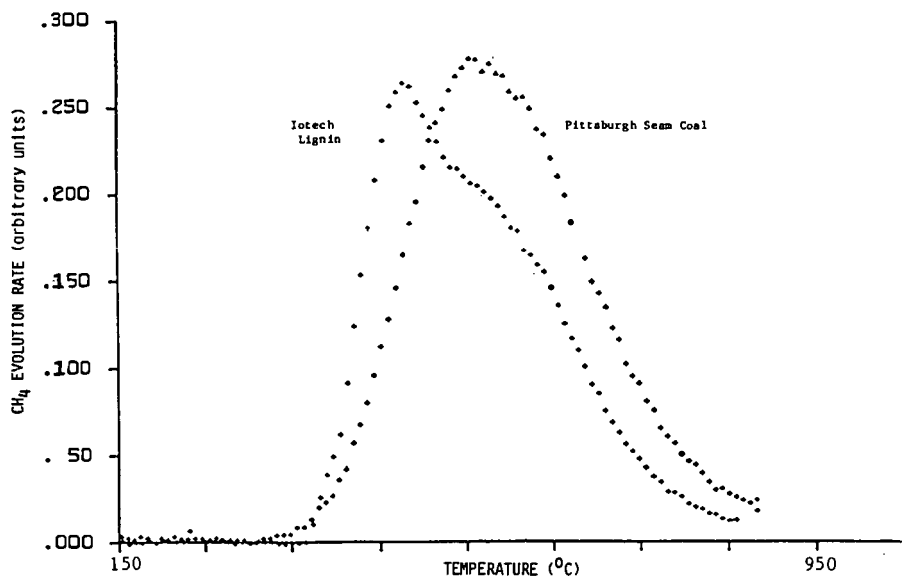
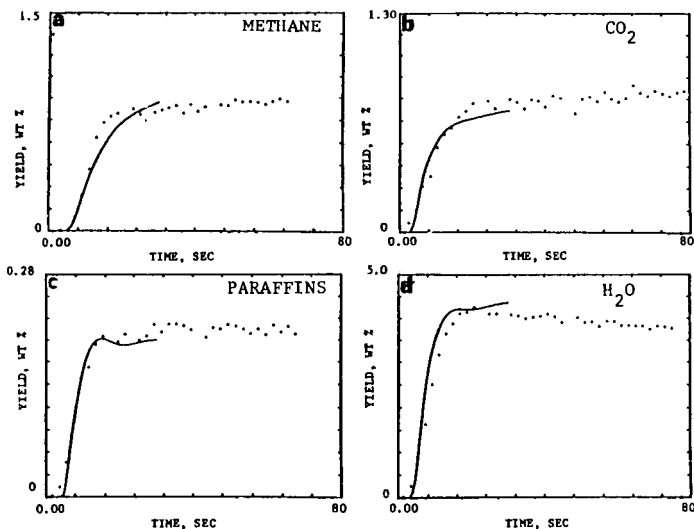Figure 8. Evolution Rate of Methane from Pittsburgh Seam Coal and Lignin at a Heating Rate of 30°C/min.

Figure 9. Major Gas Species Versus Time in a Flash Pyrolysis at 500°C, experiment (points) and simulation (solid line).